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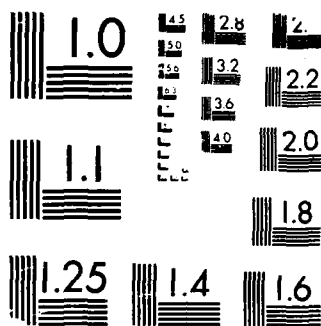
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THE OVERCHARGE BEHAVIOR OF POLYMER  
ELECTROLYTE CELLS

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ABSTRACT

The overcharge behavior of the cell  $\text{Li} | (\text{PEO})_8 \cdot \text{LiCF}_3\text{SO}_3 | \text{V}_6\text{O}_{13}$  was investigated with particular emphasis on the changes taking place at the cathode and electrolyte.

Cells placed on overcharge for long periods of time showed an inability to discharge. Optical microscopy revealed severe electrolyte and cathode degradation with the presence of white fluffy deposits located at the cathode/electrolyte interface. This was shown by EDAX analysis to be predominantly rich in salt. Vanadium was also detected at the Li-electrolyte interface.

1. INTRODUCTION

Polymer complexes formed by the reaction of an alkali metal salt and polyethylene-oxide (PEO) were first shown to be fast ion conductors at 100°C by Fenton and co-workers [1]. Subsequently a large number of groups have shown an interest in the application of these polymeric solid materials [2-6]. The encouraging results led to the use of these materials in solid state batteries as solid electrolytes [7-11].

One such material  $(\text{PEO})_8 \cdot \text{LiCF}_3\text{SO}_3$  exhibited sufficient conductivity ( $10^{-4}$  -  $10^{-3}$  @ 100 - 140°C) and electrochemical stability to be investigated further [12]. A major goal in battery research is to develop an all-solid-state rechargeable battery with the ability to store and to deliver energy efficiently and economically.

Batteries based on alkali metal anodes such as lithium and insertion cathodes such as  $\text{V}_6\text{O}_{13}$  or  $\text{TiS}_2$  have been the common systems under current study. The low equivalent weight and high negative electrode potential of lithium allow the fabrication of cells with high open-circuit voltages and high energy densities. The advantages of an all-solid-state battery have already been cited

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) <b>The overcharge behavior of the cell Li/(PEO)<sub>8</sub>-LiCF<sub>3</sub>SO<sub>3</sub>/V<sub>6</sub>O<sub>13</sub> was investigated with particular emphasis on the changes taking place at the cathode and electrolyte.</b>  <b>Cells placed on overcharge for long periods of time showed an inability to discharge. Optical microscopy revealed severe electrolyte and cathode degradation with the presence of white fluffy deposits located at the cathode/electrolyte interface. This was shown by EDAX analysis to be predominantly rich in salt. Vanadium was also detected at the Li-electrolyte interface.</b>					
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elsewhere [13]. The feasibility of this system has been tested in a variety of research cells and in some prototype hardware. Current densities of 0.1 - 1.0 mAcm<sup>-2</sup> have been reported for PEO-LiCF<sub>3</sub>SO<sub>3</sub> electrolyte cells operating at 100-140°C with energy efficiencies and specific powers of 70-80% and 100-300 Wdm<sup>-3</sup>, respectively [10].

Recent work in this laboratory has shown good cycling efficiency for Li cells utilizing (PEO)<sub>8</sub>·LiCF<sub>3</sub>SO<sub>3</sub> electrolyte and V<sub>6</sub>O<sub>13</sub> cathodes [11]. The cycle life of a cell is dependent on its mechanical and chemical stability. The parameters that influence the cycle life include depth of discharge, volumetric changes taking place in the cell, state of charge, overcharge, dendritic growth and temperature.

A knowledge of the amount of overcharge a battery can accept not only helps to ensure the attainment of full capacity of the cells, but also increases the cycle life by proper control on the degree of charge and depth of discharge in each cycle. Up to the present time, no account has been made in the literature on the effect of overcharge on this type of system. A major problem associated with overcharge is an increase in heat generation which ultimately leads to chemical and mechanical instability of the cell components resulting in a shortening in the cycle life of a battery. Hence it is important to avoid excessive overcharge in order to reduce these effects. This paper investigates the effect of cycle life and electrode/electrolyte morphology as a function of overcharge.

## 2. EXPERIMENTAL.

### 2.1. Preparation of the Cell Material and Cycling.

All handling and fabrication of the cell materials were carried out in a <1% R.H. dry room.

The solid reagents PEO (molecular weight 5 x 10<sup>6</sup>) and LiCF<sub>3</sub>SO<sub>3</sub> were pre-dried at 50°C for several days prior to use. The polymer electrolyte was prepared by dissolving a known weight of LiCF<sub>3</sub>SO<sub>3</sub> in acetonitrile (dried using molecular sieves) followed by a known weight of PEO with constant stirring. The final molar concentration of polymer to salt was 8:1. The solution was stored in a sealed bottle for 2-5 days to homogenize.

Films of the electrolyte were solution cast using the doctor blade technique. The films were air-dried for two days to ensure complete removal of the solvent followed by careful stringent drying under vacuum over P<sub>2</sub>O<sub>5</sub> for two weeks or more. Film thickness were of the order of 10-20μm.

The cathode was prepared by a complex procedure involving the materials V<sub>6</sub>O<sub>13</sub>, Shawinigan Black, PEO, lithium salt and acetonitrile. This process was adapted from a study involving the milling process, process times and particle size of the V<sub>6</sub>O<sub>13</sub>

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agglomerates and method of introduction of the lithium salt and PEO. The final dispersion was such that the particle size of the  $V_6O_{13}$  constituent was  $< 5\mu m$ . The carbon was added to enhance the electronic conductivity of the cathode element. The electrolyte phase was added to enhance the ionic conductivity and also to increase the plasticity of the cathode. Cathodes were cast from the resultant dispersion directly onto nickel foil current collector ( $\approx 25\mu m$ ) also using the doctor blade technique. Thick films in the 40-70  $\mu m$  range were obtained.

Anodes were cut from lithium foils (50  $\mu m$  thick) obtained from Foote Mineral Co.

Disc type cells [15] were assembled in the dry room. The diameter of the electrolyte, lithium and cathode was 2.86 cm. Polypropylene spacers were used to separate the two electrodes as well as hermetically seal the cell. Two electrolyte layers of about 10 $\mu m$  were employed in each cell. The cells were sandwiched between two stainless steel plate current collectors and maintained under a constant pressure using a clamping system. They were placed in an oven at 100°C.

All cells were cycled in the glove box. The theoretical capacity of the cathode was based on 8 Li intercalating into the  $V_6O_{13}$  structure. The electrode loading was about 20-30mAh for cells with about 50-70 $\mu m$  thick cathodes. In all cases a constant current discharge (C/10 rate) and a constant voltage charge through a current limiting resistor were employed.

The overcharging was conducted in a systematic manner. A typical experiment involved cycling the cell until a constant capacity was reached. The cell would then be placed on overcharge at the same rate as the discharge (namely C/10) above the nominal O.C.V of 3.2 V until a plateau was observed in the V-t curve. Once it reached the required voltage plateau, the cell would be placed at constant potential for a given time interval and the current monitored as a function of time. The cell would then be discharged at constant current to obtain the final capacity. The time interval was varied for different cells.

## 2.2 Microscopy.

Post-mortem examination was carried out on cells mainly in the charged state using both optical and scanning electron microscopy. The cells were opened in the dry room atmosphere. Each electrode and electrolyte sample was carefully peeled from one another to obtain a clean examinable surface. In some cases this was found to be more difficult than originally anticipated, so only the cross-sections were examined.

Optical micrographs were obtained using an Olympus SZIII optical microscope equipped with a polaroid camera.

Scanning electron microscopic examination was made using a JEOL 840II microscope. Low accelerating voltages were used to avoid beam damage as well as prevent sample charging. Despite this, certain Li and electrolyte specimens were found to be experiencing beam damage under the electron gun.

The cathode samples were predominantly  $\text{Li}_x\text{V}_6\text{O}_{13}$  and carbon and so were sufficiently conducting to avoid electrostatic charging by the electron beam. On the other hand, samples containing large quantities of the electrically insulating PEO could be observed directly only at low magnification because of the charging effect. In addition, the low accelerating voltages resulted in poor resolution of the micrographs. Because of these limitations only the cathode was studied in sufficient detail by SEM.

### 3. RESULTS AND DISCUSSION.

Table 1 outlines the cycling sequences for five polymer electrolyte cells. The number of cycles necessary to obtain a constant capacity was generally less than ten.

A typical cell (cell #1) was then placed on overcharge at constant current (C/10 rate) above the nominal O.C.V. of 3.2 V until it reached a plateau in the V-t curve. (This occurred at 4.95V). The cell was held at this potential and the current monitored as a function of time. At this stage the current decreased somewhat exponentially for about 1/2 h before stabilizing to some constant value. After a lapse of about 5 h, the current showed erratic behavior and then became constant. On open-circuit the cell voltage decreased to 1.2 V over a period of 2 hours.

Post-mortem examination of the cell revealed severe electrolyte and cathode degradation. Figure 1 shows an optical micrograph of the cathode containing large areas of the electrolyte. It is not totally clear from this black/white micrograph, but in actual case the electrolyte showed a marked discoloration that was clearly visible in the optical microscope. The interfacial region of the cathode-electrolyte interface was also found to be much rougher than the innermost cathode structure. In addition, certain areas of this electrolyte-cathode interfacial region showed the presence of white fluffy deposits and these were analyzed subsequently by EDAX to be predominantly rich in sulphur indicating the possibility of lithium salt,  $\text{LiCF}_3\text{SO}_3$ . Such areas are depicted in the micrograph of Figure 2.

Figure 3 shows an electron micrograph of the cathode interior. The presence of large voids is clearly evident. Furthermore, the structure is quite crystalline but somewhat fused compared to the original cathode (after casting) which appeared much finer and amorphous (no micrograph is available because of severe charging by the electron beam). The fused appearance also indicates that the structure might be less porous.

This fused structure is further exemplified by an electron micrograph of the deteriorated electrolyte shown in Figure 4. A comparison with the PEO micrograph from a normal cycled cell (Figure 5) clearly indicates large changes taking place as a result of overcharging. The normal electrolyte appears more porous and particulate.

An EDAX analysis of the cathode cross-section indicated the presence of V, S and Ni (Figure 6). In addition, an analysis of the electrolyte cross-section near the lithium electrode interface showed the presence of S, Cl, V and Ni (Figure 7). The Cl appears to originate from impurities in the PEO. It is difficult to visualize the further oxidation of  $V_6O_{13}$  since it is already in a highly oxidized state. It is more likely that the presence of vanadium in the electrolyte is caused by physical migration of the vanadium oxide particles. At 100°C, the electrolyte is already a semi-fluid and during overcharge a considerable amount of heat is developed which would result in the lowering of the viscosity of the electrolyte. This would probably be sufficient to allow such particle migration.

The detection of Ni in most cathodes and electrolytes analyzed is rather mystifying. However, recent results have shown that this now originates from the cathode current collector as a result of the oxidation process [14].

In sharp contrast, EDAX analysis of the electrolyte from a normal cycled cell (Table 1, cell #2) indicated only sulphur as expected. A typical cell examined in the charged state showed the cell components to be intact with no visible deterioration. The cathode (Figure 8) was smooth and uniform and the electrolyte maintained its original color. The white fluffy deposits found in the overcharged state were absent in this case. Furthermore there was no evidence of vanadium at the Li-electrolyte interface. This clearly suggests that vanadium is migrating as a result of the overcharging process. Figure 9 shows an electron micrograph of the charged cathode layer. The large void areas seen previously in Figure 3 are now mostly absent and the crystal structure is more platey and somewhat porous.

In order to determine the level of overcharge a cell can accept without inflicting serious damage, the cells were overcharged for lesser time intervals.

Cell #3 was charged at constant voltage to 3.2 V. On overcharge at C/10 rate, the voltage reached 5.0 V. After holding for fifteen minutes at this potential, the cell was discharged at the C/10 rate. The capacity was found to be the same as the original capacity. The cell was re-charged to 3.2 V. Examination of the cell material did not provide any evidence of cell degradation. Furthermore EDAX analysis did not show any vanadium or nickel near the Li-electrolyte interface.



The same procedure was repeated for cell #4 except that this time it was held at constant potential of 5 V for thirty minutes. Again the capacity was recovered and there was no sign of degradation nor vanadium or nickel migration.

Cell #5 was held for 1 h 20 min. at about 5 V. On open-circuit the voltage fell rapidly to 3.15 V over a period of about five minutes. Discharging at C/10 rate resulted in a capacity of only 2-3 minutes. Optical micrograph of the cathode did not show much deterioration (Figure 10) although the electrolyte consistency had changed. The electrolyte surface appeared brittle as did the lithium surface. Although the cathode at the cathode/electrolyte interface seemed intact, the cathode at the cathode/Ni interface was not. Large pittings were clearly visible in the optical microscope (Figure 11). EDAX analysis near the Li-electrolyte interface did not show the presence of Ni. so it appears that at this potential (~5 V), electrolyte degradation commences followed by degradation of the cathode and current collector.

Holding the cell at a potential of 3.2 V for several days did not degrade the cell components. A simple calculation suggests that if such a cell was left on a constant current charge then the amount of overcharge it could tolerate would only be about 15-20%. This calculation includes the time taken to reach 5V.

#### ACKNOWLEDGEMENT

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Key Words:

overcharge, microscopy	page 1
polymer, electrolyte	page 2
lithium, rate	page 3
cell, cycling	page 4
vanadium, EDAX	page 5
voltage, migration	page 6

Table 1

<u>Cell #1</u>	<u>Cell #2</u>	<u>Cell #3</u>	<u>Cell #4</u>	<u>Cell #5</u>
<p>Constant current charge above 3.2V. Plateau at 4.95V. Cell held at 4.95V and i vs t monitored. After 5h current became erratic and then was constant. On open-circuit cell voltage decreased to +1.2V over a period of 2h.</p>	<p>Normal cycled cell in the charged state.</p>	<p>Constant current charge above 3.2V. Plateau at +5V. Cell held for 15min at this potential and then discharged @ C/10 rate. Capacity recovered. Cell recharged and examined.</p>	<p>Same procedure as cell #3 except this time cell held for 30min at +5V.</p>	<p>Same procedure as cell #3 except this time cell held for 1h 20min at +5V. On open-circuit, voltage fell rapidly to +3.15V over 5min. Discharging @ C/10 rate gave 2-3min capacity.</p>

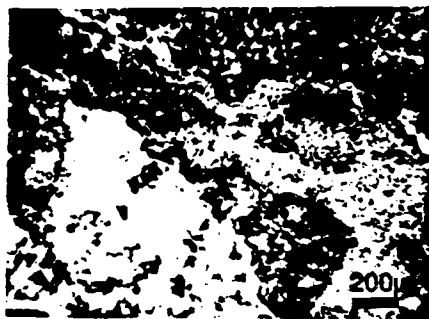


Figure 1. Optical micrograph of the cathode (cell #1) at the electrolyte/cathode interface after overcharge.



Figure 2. Optical micrograph of the cathode and electrolyte from the cathode backside (Ni side).

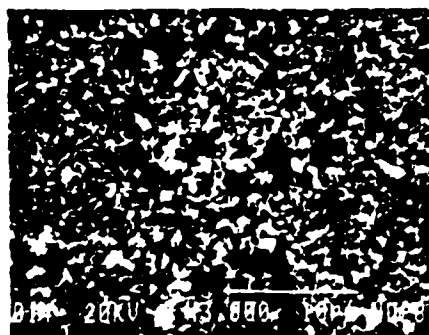


Figure 3. Electron micrograph of the cathode interior after overcharge (cell # 1).



Figure 4. Electron micrograph of the electrolyte after overcharge (cell # 1).

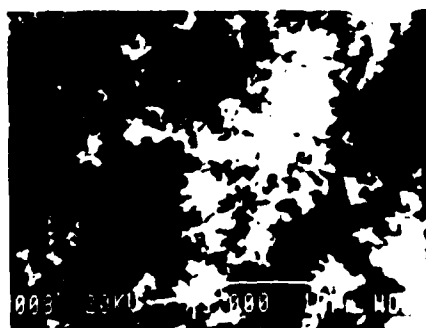


Figure 5. Electron micrograph of the electrolyte after normal charge (cell #2).

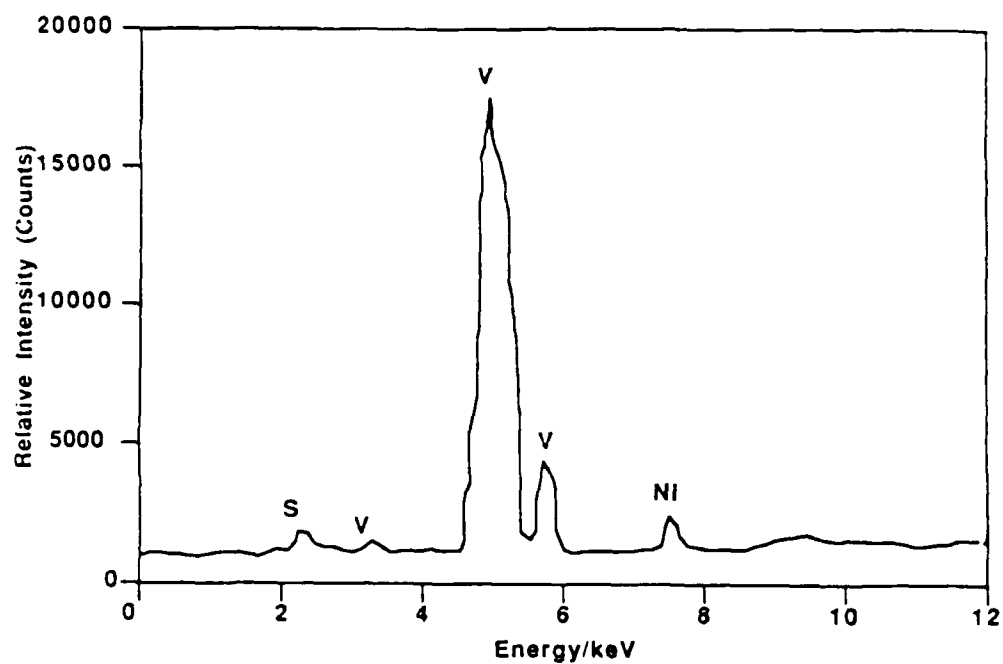


Figure 6. EDAX analysis of the cathode cross-section (cell #1).

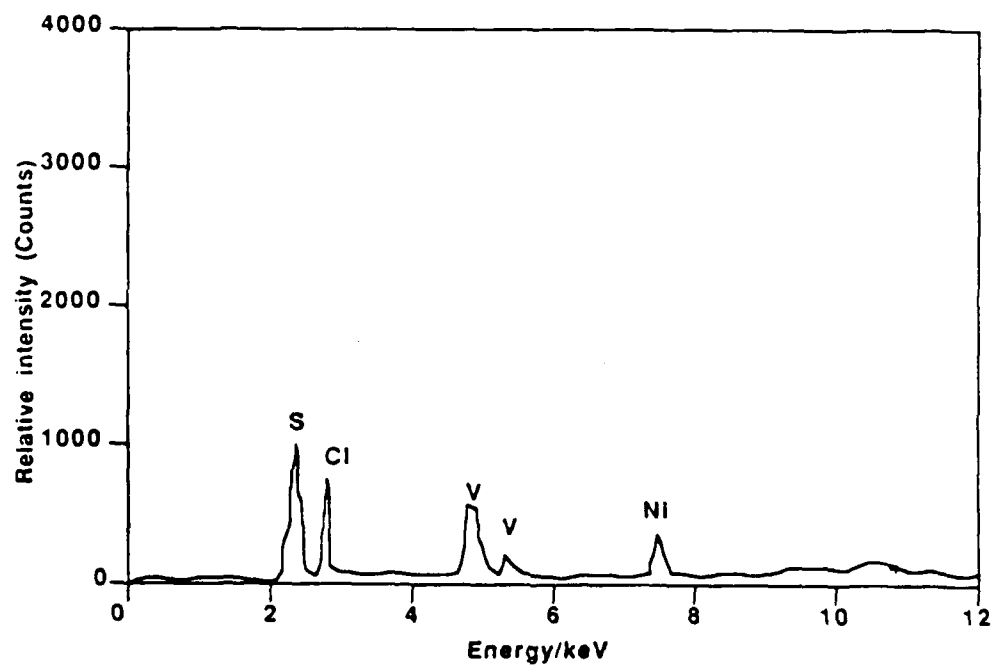


Figure 7. EDAX analysis of the electrolyte cross-section (cell #1).



Figure 8. Optical micrograph of the cathode at the cathode/electrolyte interface (cell #2).



Figure 9. Electron micrograph of the cathode interior (cell #2).

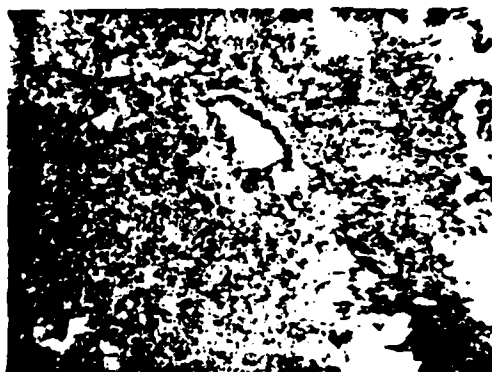


Figure 10. Optical micrograph of the cathode at the cathode/electrolyte interface (cell #5).



Figure 11. Optical micrograph of the cathode viewed from the Ni side.

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